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Effects of torrefaction process parameters on biomass feedstock upgrading

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ABSTRACT

Biomass is a primary source of renewable carbon that can be utilized as a feedstock for biofuels or biochemicals production in order to achieve energy independence. The low bulk density, high moisture content, degradation during storage and low energy density of raw lignocellulosic biomass are all significant challenges in supplying agricultural residues as a cellulosic feedstock. Torrefaction is a thermochemical process conducted in the temperature range between 200 and 300 °C under an inert atmosphere which is currently being considered as a biomass pretreatment. Competitiveness and quality of biofuels and biochemicals may be significantly increased by incorporating torrefaction early in the production chain while further optimization of the process might enable its autothermal operation. In this study, torrefaction process parameters were investigated in order to improve biomass energy density and reduce its moisture content. The biomass of choice (corn stover) was torrefied at three moisture content levels (30%, 45% and 50%), three different temperatures (200, 250 and 300 °C), and three unique reaction times (10, 20 and 30 min). Solid, gaseous, and liquid products were analyzed, and the mass and energy balance of the reaction was quantified. An overall increase in energy density (2–19%) and decrease in mass and energy yield (3–45% and 1–35% respectively) was observed with the increase in process temperature. Mass and energy losses also increased with an increase in the initial biomass moisture content.

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1. Introduction

Energy has always played an important role in life, survival, and the development of mankind. Even though it has been superseded by other more potent fossil energy sources during the last 200 years, biomass has played a major role in supplying energy since the beginning of civilization and still plays an important role in economies of developing countries. Biomass recently has received renewed attention worldwide, mainly as a consequence of high and volatile oil prices and global climate changes caused by increased fossil fuel consumption. Moreover, rapid economic growth in developing countries, high dependence on global and local transportation, pollution, depletion of sources, and endangered national security of energy importing countries have raised the awareness of the need for non-fossil based renewable energy sources [1–3]. Among renewable energy sources, such as wind, solar, geothermal, wave, tidal and ocean thermal, biomass is the most likely short term energy source with mature and readily applicable conversion technologies for the production of transportation compatible liquid fuels. Although in the long term other forms of renewable energy may supersede biomass it will still remain as the only source of renewable carbon needed for chemicals and synthetic materials production.

According to the Renewable Fuel Standard (RFS) from the Energy Independence and Security Act of 2007, the minimum annual quantity of renewable fuel in the US transportation sector should be increased from 9 billion in 2008 to 36 billion in 2022, where after 2016 most of renewable fuel must be advanced biofuel derived from cellulosic feedstocks instead of food crops [4]. In order to sustain production demanded by the RFS significant amounts of lignocellulosic biomass has to be collected, stored, and converted into biofuels.

The low bulk density, high moisture content, and low energy density of biomass feedstocks have a negative effect on the feasibility of long distance feedstock transportation. Moreover, in order to supply a feedstock for continuous operation of biorefineries year round, biomass has to be collected from large and often distant areas and hauled either to local storage facilities or to a refinery where it would be stored until conversion. Unfavorable physical properties of biomass dictate utilization of large storage facilities, which would further compromise economical use of biomass feedstock. In addition, storing such large amount of wet biomass will further increase expenses through the high rate of dry matter loss due to microbial activity and the hazard of self-heating/combustion [5–8].

Thermochemical conversion technologies, such as pyrolysis, gasification and hydrothermal processing, along with biomass co-firing in existing coal power plants, might have an important role in the production of heat energy, advanced energy carriers, chemicals, solvents, and materials. However, all aforementioned technologies have strict demands regarding the physical condition of biomass feedstocks such as particle size and shape which are

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conducive to optimal processing. Additionally the final end product characteristics and yield are also influenced by feedstock quality and composition [2]. Moreover, due to the recalcitrant nature of biomass it is difficult to grind in a continuous and cost effective manner [7]. Heterogeneity of feedstocks can also influence refinery operation considering not only different types of biomass, for example demolition wood, agricultural residues, and dedicated energy crops, or different plant species, but also the same plant species grown in different areas [9,10].

Torrefaction, sometimes also referred to as mild-pyrolysis, is a thermochemical process conducted in the temperature range between 200 and 300 °C under an inert atmosphere and low heating rate. Torrefaction is currently being considered as a biomass feedstock pretreatment particularly for thermal conversion systems. During torrefaction various permanent gases and condensables, with high oxygen content, are formed mainly due to hemicellulose degradation. As a consequence the final solid product, so called torrefied biomass, will be composed mainly of cellulose and lignin and characterized by increased brittleness, hydrophobicity, microbial degradation resistance, and energy density. Thus torrefaction can play a significant role in decreasing transportation and storage costs of biomass in the large quantities needed to sustain biofuels production. In addition, torrefaction may have positive effect on pyrolysis, gasification, and co-firing units operation by lowering power consumption and cost for biomass grinding, eliminating compounds responsible for high acidity of pyrolysis oil, and by increasing the uniformity of biomass feedstocks [9–12].

About 30 years ago, the process of torrefaction was first utilized and operated commercially for the production of a reducing agent for the metallurgical industry, but since then it has received little attention. There have been several studies that investigated the effects of torrefaction on biomass properties and the composition of different fractions released during the process, but the majority of these have focused on dry woody biomass which was finely ground before torrefaction. These experiments were conducted by utilizing either thermogravimetric analysis equipment (TGA) or small scale reactors [7,10,13,14]. Since agricultural residues will play an important role in the production of advanced biofuels more research is needed to investigate the optimum torrefaction conditions for such feedstock.

The potential for torrefaction of agricultural residues immediately after harvest without drying and before significant size reduction should be investigated in order to incorporate torrefaction early in the supply chain and maximize the benefit of the physical property changes induced through torrefaction. In this research the influence of torrefaction reaction time, temperature, and moisture content on the quantity and composition of torrefied corn stover was investigated. Quantitative and qualitative data from the analysis of solids, permanent gases, and condensable volatiles were used to investigate mass and energy flows in the torrefaction process. A Box Behnken design of experiments was utilized in this research in order to statistically model the torrefaction process in terms of mass and energy yields and evaluate the significance of temperature, time, and untreated corn stover moisture content as predictors of response variables. The results from this work will provide knowledge not only related to the influence of process parameters (time and temperature) but also the effect of moisture content of an untreated feedstock on the torrefied biomass characteristics.

2. Experimental design

2.1. Samples

Corn stover samples, harvested during the fall 2009, were obtained from Department of Agricultural and Biosystems Engineering at Iowa State University, Ames, Iowa. Corn stover biomass is a highly available agricultural residue in the Midwest and has been proposed as a feedstock for advanced biofuels production. After harvest samples were stored in a cooling chamber at 3–5 °C to prevent feedstock degradation and minimize moisture loss.

Field harvested corn stover at 22% and 41% moisture content were selected as the medium and high test moisture levels. Additional corn stover was dried to provide a suitable low moisture test level. The size of samples was reduced in a hammer mill equipped with 25 mm screen.

2.2. Torrefaction reactor

Torrefaction experiments were conducted in 2 L stainless steel fixed bed reactor with 0.1 m diameter and 0.25 m height, heated by three ceramic heaters in close contact with the reactor wall and separately controlled by PID controllers. This setup was used for coarse control of temperature, while fine temperature management was performed through circulation of preheated nitrogen gas. Fig. 1 shows the position of four thermocouples inside the torrefaction reactor used for the temperature control. Thermocouples were immersed in the biomass at four different heights (0.05, 0.1, 0.15 and 0.2 m from the bottom of reactor). They were positioned along the circumference (diameter of 0.08 m and origin at the axis of reactor) and shifted by 90° as shown in Fig. 1, top view. Nitrogen purge gas was used for maintaining an inert atmosphere during the experiments. For each experiment 4.5 L min^{-1} (0.000075 $m^3\,s^{-1}$) of nitrogen was purged through the reactor. Outlet tubing was maintained at an elevated temperature of about 200 °C to prevent condensation of released volatiles.

For the purpose of comprehensively characterizing the torrefaction of corn stover the final torrefied solid product was recovered from the process and analyzed while the volatiles released during the process as torrefaction gas were first separated into permanent gases and condensable volatiles (liquid) and then analyzed separately.

2.3. Gas analysis

Volatiles and permanent gases released from the process were cooled immediately following release from the reactor by means of glass impingers submerged in an ice bath. This facilitated removing the majority of the condensables and water from the gas sample. The remaining permanent gasses were then passed through desiccant columns before they were analyzed by a Varian 490-GC micro-gas chromatograph (Varian, Palo Alto, CA) equipped with a Molsieve 5A and Poraplot U columns.

2.4. Liquids analysis

Liquid fractions developed during the torrefaction process and collected in glass impingers were stored in the cooling chamber at 3–5 °C until they were analyzed. The water content in the condensed phase was analyzed according to the Karl–Fischer method by a moisture titrator (KEM MKS-500, Kyoto Electronics, Tokyo, Japan) and ASTM E 203-08 standard method [15]. Quantitative and qualitative analysis of organics present in condensed phase was conducted by a gas chromatograph equipped with Restek Stabilwax-DA column (Varian, Palo Alto, CA).

2.5. Proximate analysis

Torrefied biomass samples were analyzed in a thermogravimetric analyzer TGA/DSC Star System (Metler Toledo) according to a modified ASTM D 5142–04 method, in order to determine the content of moisture, volatiles, ash and fixed carbon [16]. Analysis was

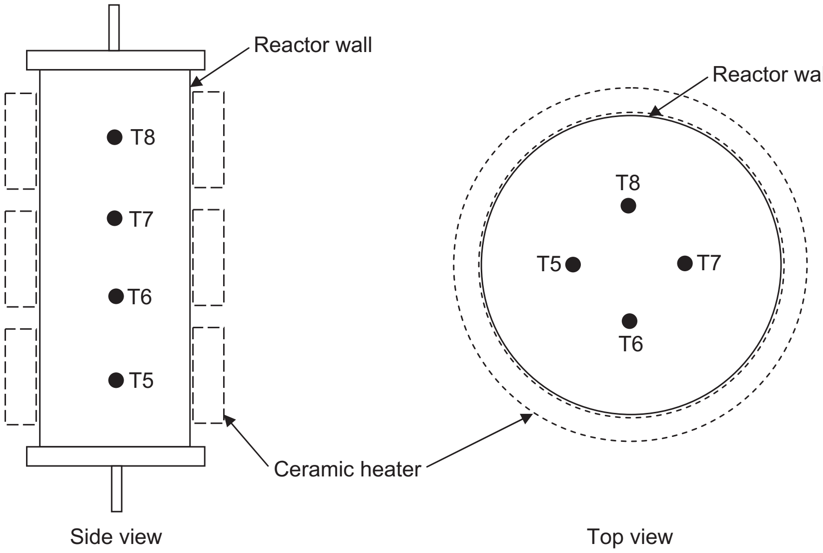

Fig. 1. Position of four thermocouples (T5, T6, T7 and T8) utilized for controlling the temperature inside the reactor (not to scale).

done under an inert atmosphere, obtained by purging nitrogen gas at flow rate of 100 mL/min. Initially samples were heated to 105 °C at the heating rate of 10 °C/min. After retaining the samples at 105 °C for 40 min, these were further heated at the rate of 10 °C/min to 900 °C, and maintained at this temperature for 20 min. Subsequently the environment was changed to oxidative by purging 100 mL/min of air for 30 min. The moisture content is determined by the mass loss after the heating period at 105 °C. Mass evolved between 105 °C and 900 °C represented volatile content, while the remaining was the fixed carbon content. The remaining after heating the sample in oxidative atmosphere at 900 °C was considered to be ash.

2.6. Ultimate analysis

Ultimate analysis of the solid fraction was done with PerkinElmer 2400 Series II CHNS/O Analyzer (PerkinElmer, Waltham, MA), according to ASTM D 5373–08 method [17]. Biomass samples were dried in an oven at 103 °C for 24 h before the ultimate analysis was conducted. Combustion was conducted at 925 °C under a helium atmosphere, while reduction was conducted at 650 °C.

2.7. High heating value determination

The higher heating value of raw and torrefied biomass samples was computed using Eq. (1) developed by Sheng and Azevedo [18].

$$\mathrm{HHV}\ (\mathrm{MJ/kg}) = -1.3675 + 0.3137\mathrm{C} + 0.7009\mathrm{H} + 0.0318\mathrm{O} \qquad (1)$$

C, percentage of carbon in biomass as determined by ultimate analysis; H = percentage of hydrogen in biomass as determined by ultimate analysis; O, percentage of oxygen determined by difference on dry and ash free basis, i.e. O (db, ash free) = 100 − C–H–N

2.8. Design of experiments

The set of torrefaction experiments conducted to meet the objectives of this project were based on a Box Behnken experimental design, which is a three level design based on the combination of a two level factorial design and incomplete block design. It is useful for statistical modeling and optimization of a response variable of interest, which is a function of three or more independent variables. Moreover, Box Behnken designs allow estimating coefficients in a second degree polynomial regression and modeling of a quadratic response surface. The response surface can be further used for process optimization, identification of maximum or minimum responses, and significance of each involved factor or their combination. Furthermore, response surfaces can be used for calculating responses not only at experimentally investigated points, but also at any point on the surface [19–21]. Three factor-three level Box Behnken design, with five replicates at the center point and 17 runs in total was used in the experiments (Table 1). JMP statistical package from SAS (SAS Institute, Cary, NC) was used for the statistical analysis of experimental data.

Table 1
Box Behnken experimental design matrix generated by JMP.

No.	Pattern	Moisture (%)	Temperature (°C)	Time (min)
1	− − 0	3	200	20
2	− 0 −	3	250	10
3	− 0 +	3	250	30
4	− + 0	3	300	20
5	0 − −	22	200	10
6	0 − +	22	200	30
7	0 0 0	22	250	20
8	0 0 0	22	250	20
9	0 0 0	22	250	20
10	0 0 0	22	250	20
11	0 0 0	22	250	20
12	0 + −	22	300	10
13	0 + +	22	300	30
14	+ − 0	41	200	20
15	+ 0 −	41	250	10
16	+ 0 +	41	250	30
17	+ + 0	41	300	20

3. Results and discussion

Process time and temperature were defined such that the torrefaction process temperature was the average of temperatures measured by four thermocouples within the torrefaction reactor during the experiment. The torrefaction start time was measured from the point when the temperature first reached the temperature proposed by the experimental design. Fig. 2 depicts an average temperature profile for one of the experiments at 250 °C.

Mass balances for the torrefaction process were computed based on the results from the solid, liquid and gas analysis, and

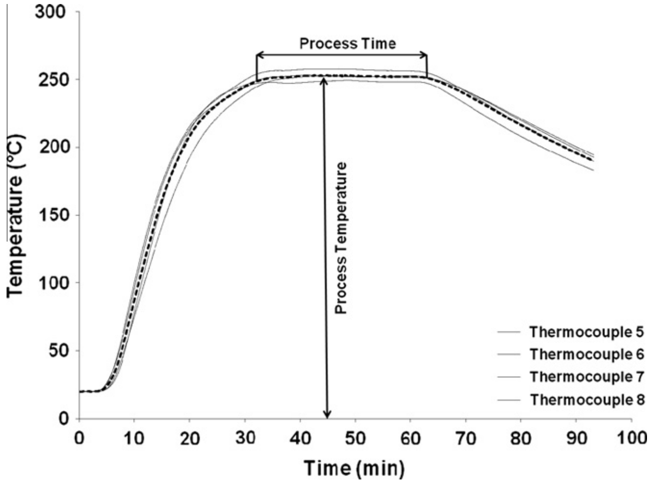

Fig. 2. Temperature profiles for four thermocouples and average temperature profile (denoted by dashed line) used to determine process temperature and time.

expressed on dry basis in the Table 2. Mass balances for torrefaction experiments conducted at low temperatures proved accurate regardless of moisture content and time. However, at 300 °C errors in mass balance occurred mainly due to the lower yield of directly weighable torrefied solids, and an increased yield of volatiles that condensed throughout the exhaust system and were hard to recover completely. Additionally, a high amount of aerosols formed at this temperature would require either electrostatic precipitators or filters to accurately account for their mass.

There was an overall trend towards a decrease in yield of solids and increase in yield of permanent gases and condensable products as both temperature and reaction time increased (Table 2). Loss in solids was much more pronounced between 250 and 300 °C, than between 200 and 250 °C, regardless of moisture content of samples. This was likely due to higher reactivity or more extensive devolatilization and decarbonization of hemicellulose fraction above 250 °C. Along with degradation of hemicellulose, initial reactions of cellulose decomposition might occur in this temperature regime, as proposed in other research [22]. The same trend was observed for the yield of condensables and permanent gases. However, at 300 °C, regardless of moisture content in raw feedstock, yield of condensables was much higher than yield of permanent gases, which might be evidence of more intensive decomposition of not only hemicellulose, but also other polymer fractions. This would support the production of heavier compounds responsible for tar formation observed in condensed phase during the experiments. There was an evident influence of moisture content on loss in mass yield at 250 °C and especially at 200 °C, where mass loss of samples with 45% moisture content was three times higher than that of samples with 3% and 22% moisture content in raw biomass (Fig. 3).

This interaction of mass loss and moisture content of the feedstock has not previously been reported in scientific journals and is of high importance for designing a commercial scale torrefaction system. A possible reason for this might be the expansion of water vapor inside the plant polymer matrix during the ramping stage of biomass heating. This expansion will loosen the material and make it less resistive to heat transfer. Since water has a higher heat conduction coefficient than both air and nitrogen it will enhance heat transfer in samples with high moisture content. Prins [23] has proposed that at heating rates lower than 50 °C/min the parameter that restricts torrefaction reaction is reaction kinetics rather than heat transfer through the particle. Nevertheless, this might not be true since the particle size in these experiments were relatively large and representative of a real agricultural residue feedstock.

Moreover, since a packed bed reactor was used in this project a higher specific heat of water vapor than nitrogen gas might increase the amount of heat delivered to the zones closer to the top of reactor and enhance degradation of biomass. Another cause might be probability of close contact between released acids with biomass structural polymers, especially hemicellulose, as a result of increased specific area caused by expansion of water vapor. According to Huber et al. [24], short chain organic acids may act as a catalyst, thus promoting mainly hemicellulose degradation at this reaction condition, but also to a lesser extent, degradation of other polymers. As a consequence of a more aggressive environment during the processing of high moisture biomass, milder conditions (temperature/time) might be used to achieve the same effect as in the case of lower moisture content biomass torrefied at more extreme conditions. Nevertheless, there was almost no difference between mass losses of different samples at the most extreme time/temperature combinations regardless of sample moisture content. This might be due to accelerated thermal degradation of cellulose and lignin, in this temperature zone, after the total amount of hemicellulose was decomposed at lower temperatures, which would ultimately eliminate any initial difference between the samples.Experimentally obtained mass loss data were analyzed using JMP statistical software and fitted into response surface quadratic model. The reduced model, containing only significant terms is shown in:

Table 2
Total mass balance for torrefaction experiments.

Sample ID	Raw biomass moisture content (%)	Process parameters		Torrefied biomass yield (%)	Condensables yield (%)	Permanent gases yield (%)
		Temperature (°C)	Time (minutes)			
3-200-20	3.2	200	20	97.1	0.02	0.4
3-250-10	3.2	250	10	86.6	1.79	1.1
3-250-30	3.2	250	30	84.4	4.07	1.4
3-300-20	3.2	300	20	57.4	13.30	2.7
22-200-10	22.1	200	10	98.1	0.39	0.5
22-200-30	22.1	200	30	98.4	0.40	0.6
22-250-20	22.1	250	20	86.2	4.32	1.3
22-250-20	22.1	250	20	85.3	4.37	1.3
22-250-20	22.1	250	20	83.4	4.39	1.5
22-250-20	22.1	250	20	83.5	4.26	1.4
22-250-20	22.1	250	20	83.4	4.09	1.4
22-300-10	22.1	300	10	58.0	11.52	2.0
22-300-30	22.1	300	30	53.9	18.39	3.3
41-200-20	41.0	200	20	91.2	0.66	0.6
41-250-10	41.0	250	10	80.0	3.79	1.2
41-250-30	41.0	250	30	78.7	6.11	1.3
41-300-20	41.0	300	20	56.3	18.59	2.9

$$\text{Predicted mass loss} = 95.68 - 1.0396 * \text{temperature} + 0.2491 * \text{moisture} + 0.00284 * (\text{temperature})^2 \quad (2)$$

where temperature, °C and moisture, wt.%db.

The summary of fit and analysis of variance are included in Tables 3 and 4 respectively. As can be seen from Table 3 the mass loss response surface model is in good agreement with actual data obtained in experiments.

According to the model, temperature, moisture, and temperature squared were the only significant parameters (Table 5). The strength of effect of two significant process parameters on the dry matter mass loss is better revealed by surface plot in Fig. 4. The effect of the moisture content of the raw biomass on dry matter loss is depicted in the plot by the more pronounced curvature in the temperature region below approximately 260 °C and moisture content above about 20%.

As revealed by Fig. 5, water represents the largest portion of condensables released during the torrefaction process, followed by acetic acid, furfural, methanol, and hydroxyacetone in much smaller quantities. The water represented in Fig. 5 is only reaction water and does not include water associated with the initial moisture content of the biomass. Water is formed in the process of polymer dehydration through the release of hydroxyl groups while acetic acid and methanol are formed from acetoxy and methoxy groups attached to hemicellulose sugar monomers and lignin. Other compounds are generated at high temperatures by thermal decomposition of plant polymer monomers [11]. As can be seen in Fig. 5, the amount of condensables released during torrefaction of biomass samples with initial moisture content of 22% and 41% are not significantly different. However, they are two times higher than in the case of torrefaction of samples with 3% initial moisture content.

Fig. 6 shows the composition of permanent gas phase released during the torrefaction of biomass with different initial moisture contents and at various combinations of process parameters. In Fig. 6, only carbon monoxide and carbon dioxide are shown, since these are the main gas components even though traces of methane and hydrogen are present at high reaction temperature. As can be seen in Fig. 6, the ratio of carbon monoxide and carbon dioxide increases with the increase in both temperature and time. This is different from the influence of time on mass yield which does not have a significant effect. The composition of the permanent gas phase is not affected significantly by moisture content in raw feedstock. Production of carbon dioxide during the process might be explained by decarboxilation of acid groups attached to hemicellulose, while carbon monoxide may be produced in the reaction of carbon dioxide and steam with char at high temperatures [25].

Fig. 7 shows the results of the proximate analysis of corn stover torrefied at different treatment conditions. As can be seen in Fig. 7, temperature has the strongest effect on torrefied biomass composition. Moreover, as the temperature increases the amount of fixed carbon follows the same trend and rises from about 1.5 up to 3 times, at 250 °C and 300 °C respectively, relative to untreated biomass. This is a consequence of the more extensive removal of hydrogen and oxygen from biomass, although some carbon will be released in the form of hydrocarbons. There is a trend in the reduction of volatiles content by about 30% at the highest temperature as a result of aforementioned changes in biomass composition. This torrefied material will produce less organic compounds and aerosols during combustion and has a higher heating value. Water content of torrefied corn stover determined during proximate analysis was water adsorbed by biomass while it was waiting for the analysis in the TGA's autosampler.

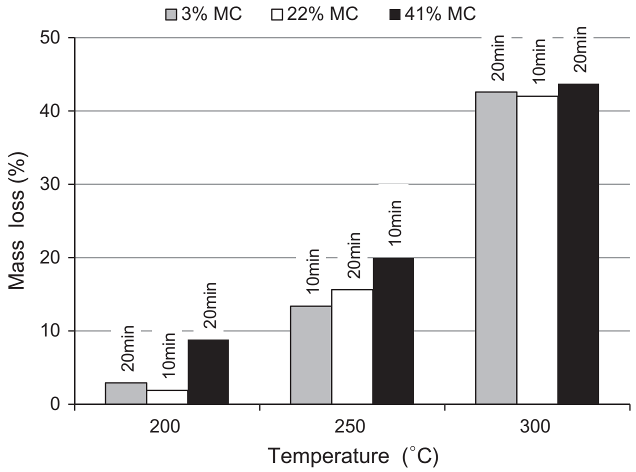

Fig. 3. The effect of untreated biomass moisture content on mass loss of torrefied samples.

Table 3
Summary statistics for the mass loss response surface model with three predictors: moisture, temperature and time.

R^2	0.993
R^2 adjusted	0.985
Root mean square error	1.807

Table 4
ANOVA for the mass loss response surface model with three predictors: moisture, temperature and time.

Source	DF	Sum of squares	Mean square	*F* ratio	Prob. >*F*
Model	9	3465.10	385.01	117.82	<0.0001*
Error	7	22.87	3.268		
Corrected total	16	3487.97			

* Significant.

Table 5
List of all terms used to obtain mass loss and energy yield models and their respective *p* – values.

	Mass loss model	Energy yield model
Term	Prob. > |*t*|	Prob. > |*t*|
Intercept	<0.0001*	<0.0001*
Time	0.1964	0.3783
Temperature	<0.0001*	<0.0001*
Moisture	0.0069*	0.0025*
Time × temperature	0.2630	0.4481
Time × moisture	0.8106	0.8937
Temperature × moisture	0.2260	0.4481
$(\text{Time})^2$	0.8546	0.6227
$(\text{Temperature})^2$	<0.0001*	0.0002*
$(\text{Moisture})^2$	0.0848	0.0211*

* Significant terms (determined by JMP statistical package).

Torrefaction increases the amount of atomic carbon while decreasing the amount of atomic hydrogen and oxygen as shown in Table 6. A consequence of this change in the chemical composition was a decrease in the atomic O/C and H/C ratio of torrefied biomass in comparison to raw biomass. This is due to the release of volatiles rich in hydrogen and oxygen, such as water and carbon dioxide. The decrease in O/C, regardless of the moisture content in the raw biomass, can be up to about 7%, 15% and 45% at 200, 250 and 300 °C respectively. This change in the chemical composition

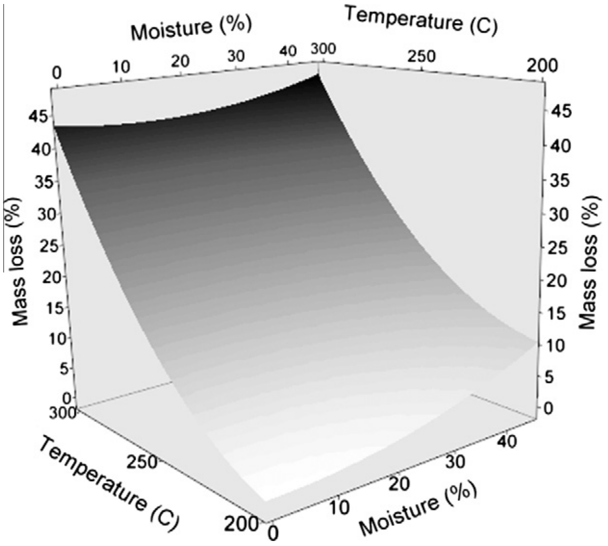

Fig. 4. Surface plot of the effect of temperature and moisture content of raw biomass on predicted mass loss (time = 20 min).

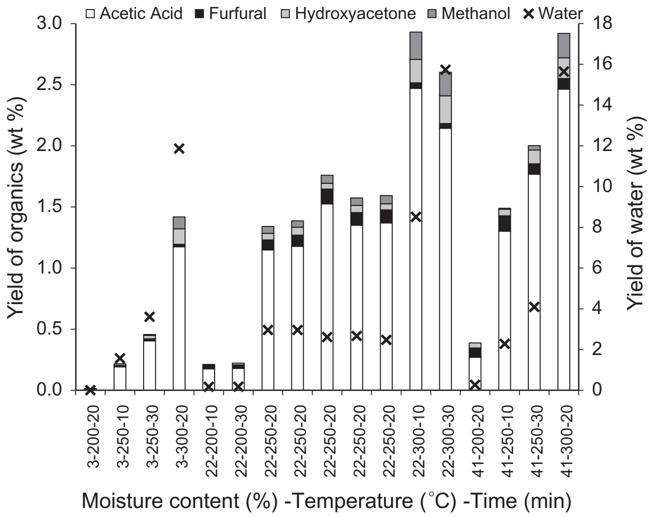

Fig. 5. Composition of condensable volatiles released during torrefaction. The amount of water produced in torrefaction reaction and condensed together with organics was determined as a difference between the total water content in condensable phase and initial biomass moisture content. Only the reaction water is shown in Fig. 6.

of biomass will improve its quality as an energy source through an increase in energy density since more oxygen than carbon is lost in the form of volatiles.

Another important characteristic of torrefied corn stover is its increase in energy density when compared to raw biomass. This is the result of a decrease in mass of torrefied samples through the release of compounds rich in oxygen and hydrogen. It can be seen in Fig. 8 that temperature has strongest impact on energy density of torrefied biomass, while the effect of time and moisture is much less expressed.Energy yield per dry raw biomass indicates the total energy preserved in the torrefied biomass. It was computed from mass yield and higher heating values using Eq. (3) and expressed as a percentage of energy content of untreated dry biomass.

$$E_{\text{Yield}}(\%) = (m_{\text{torrefied}}/m_{\text{initial}})_{\text{dry basis}} * E_{\text{torrefied}}/E_{\text{initial-dry basis}} \tag{3}$$

$m_{\text{torrefied}}$, mass of biomass feedstock measured after torrefaction expressed on dry basis; m_{initial}, mass of untreated (raw) biomass feedstock measured before torrefaction expressed on dry basis; $E_{\text{torrefied}}$, specific energy content of biomass feedstock after torrefaction expressed on dry basis; $E_{\text{initial-dry basis}}$, specific energy content of biomass feedstock before torrefaction expressed on dry basis.

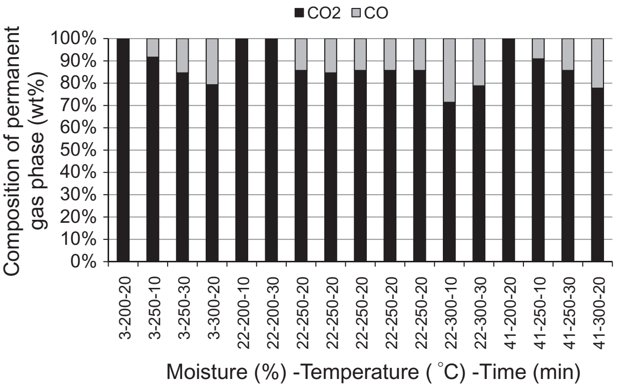

Fig. 6. Change in permanent gas composition with process parameters and raw biomass moisture content.

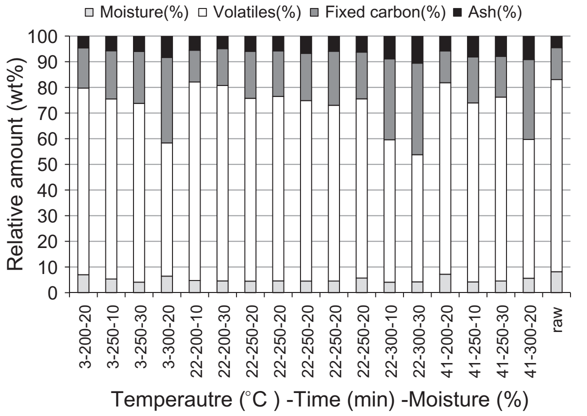

Fig. 7. Proximate analysis of torrefied and raw corn stover.

Energy yields computed using Eq. (3) are shown in Fig. 9.

These values were fitted to response surface model represented by Eq. (4), in order to analyze the effect of process parameters on energy yield.

$$\begin{aligned} \text{Predicted energy yield} = {} & 10.0379 - 0.0144 * \text{moisture} \\ & + 0.9278 * \text{temperature} \\ & - 0.00721 * (\text{moisture})^2 \\ & - 0.002461 * (\text{temperature})^2 \end{aligned} \tag{4}$$

where temperature, °C and moisture, wt.%db.

As shown in Table 7 and Table 8, the model (Eq. (4)) was in good correlation with the actual data as justified by relatively high R^2 values (a measure of the amount of deviation around mean explained by the model). The small p-value in the ANOVA indicates high model significance.

In this model (Eq. (4)) the significant parameters are temperature, temperature squared, moisture and moisture squared (Table 5). As revealed in Fig. 10, biomass torrefied at lower temperatures has the highest energy yield, which was expected since this parameter was strongly dependant on mass yield which was significantly affected by process temperature. Moisture has much less influence on energy yield than temperature as seen in Fig. 10.

However, the initial moisture content induced up to 10% more energy loss at temperatures below 220 °C and raw biomass

Table 6
Ultimate analysis and computed energy density of torrefied samples.[a]

Sample	C (wt.%)	H (wt.%)	N (wt.%)	O[b] (wt.%)	HHV[c] (MJ/kg)
3-200-20	45.8	5.5	0.5	48.2	18.4
3-250-10	47.7	5.3	0.6	46.4	18.8
3-250-30	49.1	5.4	0.6	45.0	19.2
3-300-20	58.7	4.7	0.7	35.8	21.5
22-200-10	45.7	5.7	0.7	47.9	18.5
22-200-30	45.8	5.5	0.6	48.1	18.4
22-250-20	49.1	5.4	0.7	44.8	19.2
22-250-20	48.3	5.5	0.6	45.6	19.1
22-250-20	49.2	5.4	0.7	44.7	19.3
22-250-20	49.4	5.4	0.6	44.5	19.3
22-250-20	48.7	5.4	0.6	45.3	19.1
22-300-10	56.6	4.9	0.9	37.6	21.0
22-300-30	59.0	4.7	1.0	35.4	21.6
41-200-20	45.6	5.4	1.0	48.0	18.2
41-250-10	48.2	5.3	0.9	45.6	18.9
41-250-30	48.8	5.2	0.9	45.1	19.0
41-300-20	55.8	4.8	1.1	38.2	20.8
Raw	44.2	5.8	0.5	49.5	18.2

[a] Sulfur levels for all analyzed samples were at levels lower than analyzer's precision level and were discarded as uncertain.

[b] Determined by difference.

[c] Calculated.

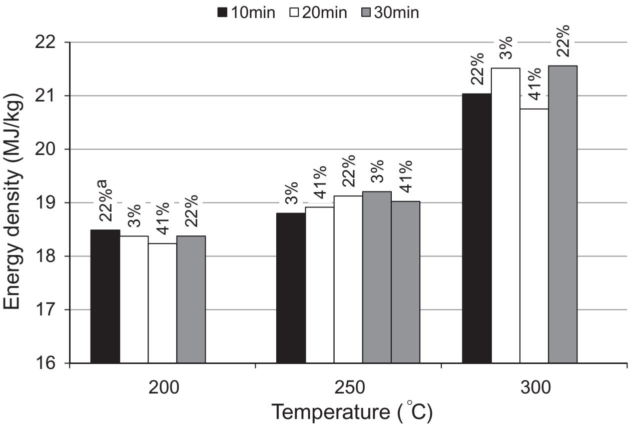

Fig. 8. Effect of process parameters and raw biomass moisture content on energy density of torrefied material. [a]Raw biomass moisture content (wet basis).

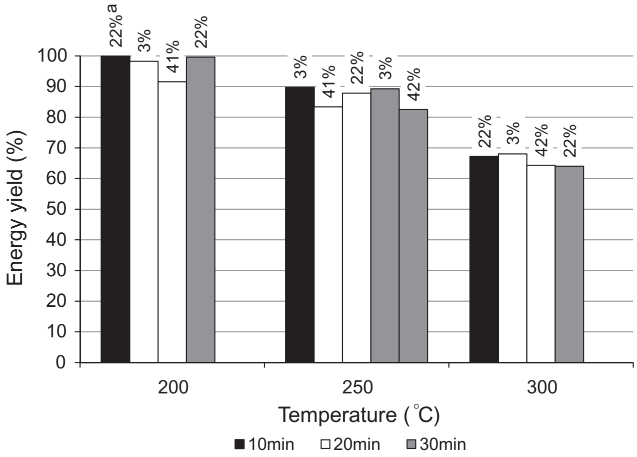

Fig. 9. Effect of process parameters and initial moisture content of untreated biomass on energy yield. [a]Raw biomass moisture content (wet basis).

moisture content higher than 20%. This was correlated with mass loss and was justified by the similar contour plot curvature in Fig. 4. Moreover, as displayed in Fig. 10, moisture had a stronger influence on energy yield than on mass loss, even at 300 °C. This might be due to the loosening effect of water on fibrous matrix, its role in polymer hydrolysis, and formation of organic acids that promotes more extensive cellulose and lignin degradation through high energy volatile compounds, such as tar.

Table 7
Summary statistics for the energy yield response surface model with three predictors: moisture, temperature and time.

R^2	0.989
R^2 adjusted	0.977
Root mean square error	1.804

Table 8
ANOVA for the energy yield response surface model with three predictors: moisture, temperature, and time.

Source	DF	Sum of squares	Mean square	*F* ratio	Prob. >*F*
Model	9	2253.06	250.341	76.88	<0.0001[*]
Error	7	22.79	3.256		
Corrected total	16	2275.86			

[*] Significant.

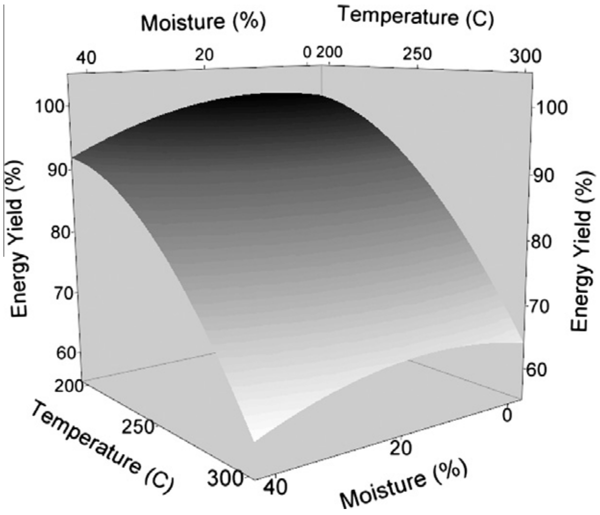

Fig. 10. Surface plot of the effect of temperature and moisture content of raw biomass on predicted energy yield (time = 20 min).

4. Conclusion

Corn stover undergoes changes in chemical composition, mass, and energy content during the torrefaction process. As expected these changes were more extensive at high temperatures and characterized by mass loss of up to 45% as well as a decrease in the O/C ratio from 1.11 to 0.6 and an increase in the energy density of about 19%. However, high mass loss offset gain in energy density and significantly reduced overall energy yield. Moisture content had a significant effect on energy density, mass and energy yield, and generally induced a reduction in each of these parameters. Moreover, the effect of moisture is more pronounced at lower temperatures, where if moisture content in raw biomass is increased from 22% to 44%, energy yield could be reduced by about 10%. Nevertheless, there is a raw biomass moisture content window between 3% and approximately 20% that can allow for the use of corn stover feedstock directly from the field without any negative effect on energy yield.

Despite inevitable losses in energy yield during the process, additional research in the future might justify the use of torrefaction as a biomass pretreatment or upgrading step, by obtaining data that will prove savings in torrefied biomass particle size reduction, improvements in storage stability, hydrophobicity, and chemical properties important for thermochemical processes, such as pyrolysis, gasification, and co-firing.

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